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Master equations for the micro-states description of carrier relaxation and recombination in quantum dots

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Abstract. Modeling of time resolved experiments on zero-dimensional quantum dots requires a conceptually different approach than for higher dimensional semiconductors. A description via master equations for the micro-states is necessary since quantum dots behave as independent objects. The impact of finite inter-level relaxation time is included in our model. Description via conventional rate equations for population probabilities averaged over the dot ensemble is inadequate. Two different time resolved luminescence experiments for quantum dot systems with fast and slow inter-level relaxation, respectively, are modeled to provide typical applications of our approach.

The energy relaxation and recombination of charge carriers in three-, two- and one-dimensional semiconductors has been investigated to great extent, e.g. Ref. [1–3]. Common to materials with these dimensionalities (bulk, quantum wells, quantum wires) is, that their properties can be adequately described by *continuous* charge carrier *densities* n and p for electrons and holes, respectively. The probabilities of events in the charge carrier gas are essentially dependent on the product of such densities, e.g. np for inter-band recombination and n^2p or np^2 for the Auger effect.

With the advent of semiconductor quantum dots (QDs) fabricated by self-organized growth [4–6] zero-dimensional electronic systems with well controlled properties and area densities of 10^9 to 10^{11} cm^{-2} became available. Such QD layers represent systems *qualitatively different from any higher dimensional semiconductor structure*. The carriers in individual QDs populate discrete levels and are described by *integer numbers*. The probability of events does not depend on the *average* carrier density but on the condition whether the event partners are simultaneously present in a particular QD. Despite this rather obvious fact, up to now only conventional rate equations (CRE) for the ensemble averaged level occupations, inspired by the description of bulk material or quantum wells, have been used to model carrier dynamics in QD ensembles [7–10]. The tremendous experimental interest in the carrier dynamics in quantum dots [7–16] is due to the concern about the general usefulness of QDs for high speed operation of devices, like lasers or light emitting diodes, because capture and inter-level relaxation processes might be slow.

In this work we will show that CRE fail for the description of QD systems. A conceptually fundamentally different model is presented, namely master equations for all micro-states (MEM) of the QD. A micro-state of the QD represents one particular occupation with carriers; the entirety of all micro-states represents the phase space. Such an approach has been used for the description of the Auger process for the spin-degenerate ground state of CdS micro-crystals in a glass matrix [17] and spin dynamics

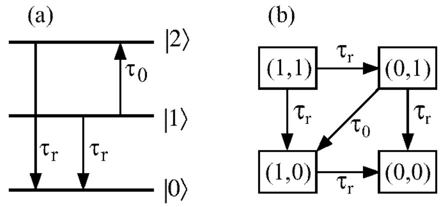

Fig 1. Schematic representation of the conventional rate equation model (CRE) and the master equation for the micro-states (MEM) for a two-level system.

of the ground state of (two-dimensional) excitons [18], both involving four micro-states. However, to the best of our knowledge, multi-level systems and inter-level relaxation have not been described using micro-states. An alternative approach are Monte-Carlo simulations [19] which are harder to implement, are much more time consuming and do not yield quasi analytical results. Using the MEM approach we will model actual time-resolved experiments on two fundament ally different QD systems: Small InAs/GaAs pyramids [6, 20] and strain induced quantum dots [10, 21], with fast and slow inter-level relaxation time constants, respectively.

In order to illustrate why CRE models fail in general to describe recombination from layers of decoupled QDs we compare the CRE and the MEM models for a simple two-level system. We assume two non-degenerate electron-hole pair (eh-pair) levels $|1>$ and $|2>$ which can both decay radiatively with the same time constant τ_r (Fig. 1). If in a dot level $|2>$ is occupied and level $|1>$ is empty, an inter-level relaxation process can occur with a time constant τ_0. In the CRE model the system is described by population probabilities f_1 and f_2 for the levels, respectively, taking values $0 \leq f_i \leq 1$. The rate equations (after preparation of an initial non-equilibrium population and switch-off of any external excitation) are

$$\frac{df_1}{dt} = -\frac{f_1}{\tau_r} + \frac{f_2(1-f_1)}{\tau_0} \tag{1}$$

$$\frac{df_2}{dt} = -\frac{f_2}{\tau_r} - \frac{f_2(1-f_1)}{\tau_0} \tag{2}$$

The second term in both equations is used to model the inter-level scattering and contains a factor $1 - f_1$ for the available empty states to describe the “Pauli blocking”. The final state population must be considered for quantum dots, while it is usually neglected in CRE models for quantum wells [22, 23].

A correct description of the QD ensemble is achieved using all micro-states. In our example these are dots with the two levels filled with (n_1, n_2) eh-pairs, i.e. (0,0) for empty dots, (1,0) and (0,1) for dots where either the $|1>$ or the $|2>$ level is filled, and (1,1) for completely filled dots. The probabilities to find a dot with a specific micro-state in the ensemble shall be given by w_{00}, w_{10}, w_{01}, and w_{11} with $w_{00}+w_{10}+w_{01}+w_{11} = 1$. The master equations for the possible transitions between the micro-states (Fig. 1) are

$$\frac{dw_{00}}{dt} = \frac{w_{10}}{\tau_r} + \frac{w_{01}}{\tau_r} \tag{3}$$

$$\frac{dw_{10}}{dt} = -\frac{w_{10}}{\tau_r} + \frac{w_{11}}{\tau_r} + \frac{w_{01}}{\tau_0} \tag{4}$$

$$\frac{dw_{01}}{dt} = -\frac{w_{01}}{\tau_r} + \frac{w_{11}}{\tau_r} - \frac{w_{01}}{\tau_0} \tag{5}$$

$$\frac{dw_{11}}{dt} = -2\frac{w_{11}}{\tau_r} \tag{6}$$

The term w_{01}/τ_0 describes the inter-level relaxation. We note that "Pauli blocking" is not explicitly introduced; implicitly it is included by not considering "overfilled" micro-states like (2,0). The issue of how to model finite state population does not arise in the MEM scheme.

The population probabilities f_1 and f_2 used in the conventional rate equation approach can be expressed as $f_1 = w_{10}+w_{11}$ and $f_2 = w_{01}+w_{11}$. The inter-level scattering term in the CRE description translates into

$$\frac{f_2(1-f_1)}{\tau_0} \rightarrow \frac{(w_{01}+w_{11})(w_{01}+w_{00})}{\tau_0} \tag{7}$$

which is obviously unreasonable. The term is quadratic in w_{01} and includes, due to the ensemble averaging procedure, empty (w_{00}) and completely filled (w_{11}) dots which do not contribute to the inter-level scattering process at all.

For $\tau_0 = 0$ (and complete initial filling, i.e. $f_2(t=0) = f_1(t=0) = 1$ and $w_{11}(t=0) = 1$, respectively) the CRE model yields a non-exponential transient for the excited state and a kink at $t = \tau_r ln(2)$ in the transient of the ground state. The decay of the excited state occurs too fast in the CRE model for $\tau_0 < \tau_r$ and a false value $\tau_0 \approx \tau_r$ will be obtained from a fit with CRE. CRE models are in principle inadequate for the description of QDs. Their application for the determination of inter-level scattering times from time resolved luminescence experiments can lead to wrong results.

In our theoretical model we use the following assumptions, which are valid for strongly confined carriers: The single particle levels $n = 1, 2, \ldots$ of the QDs are populated with electrons and holes; $n = 1$ is also referred to as ground state, $n = 2$ as first excited state. The maximum number of carriers on a given level is determined by the degeneracy g_n of the level. Electrons and holes recombine radiatively between single particle states, i.e. Coulomb correlation is neglected. However, also a representation in the exciton picture could be chosen. The transitions are denoted by the electron and hole levels involved, e.g. 1e-1h or 2e-2h. As a consequence, the lifetime of the biexciton (dot filled with two electrons and holes in their single particle ground state, $XX \rightarrow X + \gamma$) is given by $\tau_{XX} = \tau_X/2$, τ_X denoting the lifetime of a single eh-pair in the ground state. Two-photon processes ($XX \rightarrow 2\gamma$) and Auger recombination are neglected. Throughout the paper the low temperature case is treated where excited states are not thermally populated.

The inter-level scattering is described by the time constant τ_0 for one single relaxation process between any two non-degenerate levels. Thus the relaxation rate between micro-states scales with the number of available initial and final states and becomes larger for higher excited states. The transition rate of an eh-pair in an excited state into the empty spin-degenerate ground state shall be $2/\tau_0$. If spin-conserving relaxation processes dominate, as suggested in Ref. [24] at least for moderate magnetic fields, the number of available final states would be only one; in this case $\tau_0/2$ must be interpreted as the inter-level scattering time. A more detailed model than presented here including detailed spin dynamics, also taking into account dark exciton states [24, 25], can be

derived on the basis of our multi-level MEM concept. It will be subject to subsequent work and needs additional experimental input on spin scattering rates in QDs.

First we predict the asymptotic decay constants (at long times after excitation) of QD excited state luminescence transients using the MEM model for the case that the ground state was initially filled. For $\tau_0 = 0$ the carriers populate always the energetically lowest possible states. The asymptotic transient of the first excited state is then governed by dots in the $(2, 1, \cdots)$ state. This micro-state obviously decays with the time constant $1/\tau_{(2,1)} = 1/\tau_r^2 + 2/\tau_r^1$, where τ_r^2 (τ_r^1) denotes the recombination time constant of the 2-2 (1-1) transition. For finite values of τ_0, the asymptotic decay constant τ_∞^2 of the first excited state is given by eq. 8 in the MEM model:

$$\frac{1}{\tau_\infty^2} - \frac{1}{\tau_r^2} = \frac{2}{\tau_r^1} \quad \text{for} \quad \tau_0 < \tau_r^1, \quad \frac{2}{\tau_0} \quad \text{for} \quad \tau_0 \geq \tau_r^1 \tag{8}$$

A finite value of τ_0 has only an impact on the asymptotic transient of the excited state for $\tau_0 > \tau_r$ (for CRE the lower formula is valid for all values of τ_0). However, for $\tau_0/\tau_r \approx 1$ the true asymptotic values are only reached for large delay times; for the typical dynamic range $10^1 - 10^4$ of time resolved luminescence experiments numerical evaluation is needed.

The level structure of small pyramidal self-organized InAs/GaAs QDs has been analyzed [20, 26]. The multi-phonon relaxation mechanisms present in such dots have been discussed [27]. Here, we will analyze time resolved experiments where the hole ground and excited state become populated. The transitions with ground state electrons are labeled 1e-1h and 1e-2h. Both hole levels are spin-degenerate, thus $3 \times 3 = 9$ micro-states have to be included in the MEM. Our model shall contain only four physical parameters: the recombination time constants for both transitions τ_{1e-1h} and τ_{1e-2h} (the excited state is affected by a non-radiative recombination channel [27] and is thus expected to have the shorter time constant), the inter-level scattering time τ_0 and the time constant τ_c describing the capture of carriers from the barrier into any level of the QD. We use $\tau_c/\tau_{1e-1h} = 0.01$ to generate transients with the experimental ly observed fast onset [15, 13]. Coulomb scattering is argued to shorten the capture process [12, 13].

Since the peaks of the two transitions overlap spectrally [20], at long delay time the temporal behavior of the luminescence detected at the energy of the excited state is given by that of the ground state. In Fig. 2 the measurement is shown together with several fits. In experiments with resonant excitation of the excited state [15], the (initially empty) ground state exhibits a rise time of 30 ps, which is a direct measurement of the fast inter-level relaxation constant. A fit of the transient for non-resonant excitation using $\tau_0 = 30$ ps yields a perfect fit of the transients for the MEM approach ($\tau_0/\tau_{1e-1h} = 0.04$). We note that the fit is practically identical for any value $\tau_0 < 100$ ps including $\tau_0 = 0$ ps. The decay of non-resonantly excited transients is found to be insensitive to the inter-level relaxation constant if it is small (as is clear from eq. 8) and thus unsuited for its determination. The (2,1) micro-sta te with a filled ground state governs the decay of the excited state in the InAs/GaAs pyramids. Using CRE an erroneous value of about $\tau_0 = 240$ ps is necessary in order to fit the experimental data for the excited state transition. The decay of the excited level in the CRE scheme is too fast for small values of τ_0; a relatively sharp bend occurs in the transient, indicated by the arrow in Fig. 2.

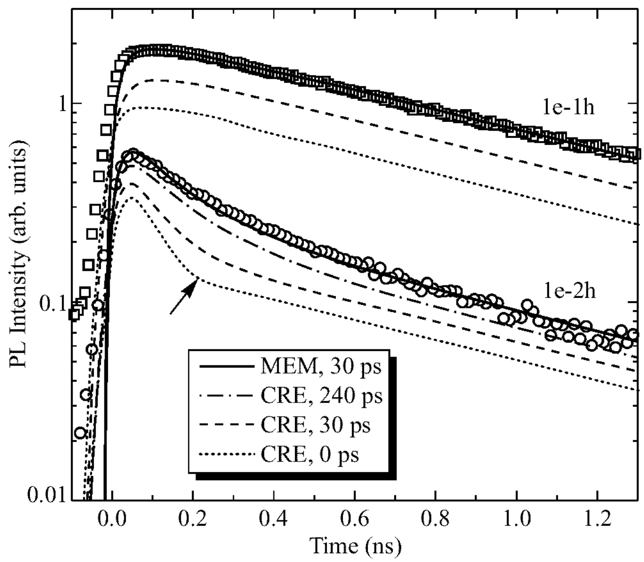

Fig 2. Experimental transients of the ground (1e-1h) and excited state (1e-2h) transition in InAs/GaAs quantum dots (symbols). Solid lines: Fit with MEM model, other lines (vertically shifted): fits with CRE model using different values for τ_0 as given in the figure. For all transients $\tau_{1e-1h} = 0.85\ ns$ and $\tau_{1e-2h} = 0.24\ ns$ have been used. The arrow denotes the unrealistic sharp bend in CRE transient for small values of τ_0.

Time resolved experiments on strain induced dots [21] have been reported in Ref. [10] (Fig. 3b). The electronic level structure of such dots is well described by a two-dimensional harmonic oscillator model, exhibiting $K = 5$ levels for electrons and holes with degeneracies $g_n = 2n$, $n = 1, \cdots, K$. Self-organized QDs, grown by a Stranski-Krastanov process, with similar five-level structure were reported [8]. The total number of states is $M = \sum_{n=1}^{K} g_n = 30$; the number of distinguishable micro-states is $\prod_{n=1}^{K}(g_n + 1) = 10395$. Each micro-state is unambiguously described by a quintuple $(n_1, n_2, n_3, n_4, n_5)$, $0 \leq n_i \leq g_i$. Radiative transitions are allowed between electrons and holes with the same quantum numbers, i.e. 1e-1h, 2e-2h. In the following we assume that the excess carriers have been deposited in the barrier via a short pulse at $t = 0$. The onset of the transients will be modeled with $\tau_c = 4$ ps as recently determined by up-conversion experiments using the same excitation intensity [28]. This onset is faster than the time resolution of the streak camera experiment shown in Fig. 3b and our simulations do not attempt to fit the onset. The saturation value of intensity from the four lines scales like 2:3.4:5.3:7.5 and is not exactly given by the degeneracies which would predict 2:4:6:8. We believe that this effect is caused by non-identical radiative lifetimes of eh-pairs on the different levels and include this fine-tuning for the quantitative fit by using recombination time constants τ_{ne-nh} which scale like 1:1.17:1.12:1.06. For the 5e-5h transition (not measured) we assume a factor of 1.1.

For finite τ_0 the different inter-level scattering processes entering the model have to be distinguished. We will compare two "trickle down" models: "TDA": scattering processes are allowed to *all* lower levels $n \rightarrow n-1, \cdots, 1$ and "TDN": scattering

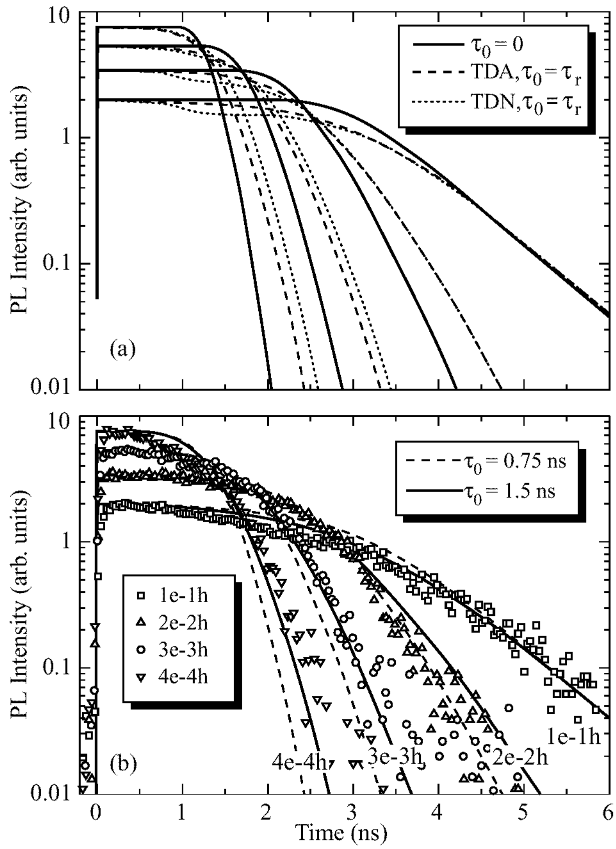

Fig 3. Transients for five-level quantum dots and master equation model. (a) Comparison of theoretical transients for instantaneous relaxation ($\tau_0 = 0$) and TDA and TDN model for $\tau_0 = \tau_{1e-1h}$. (b) Experimental data and fit with TDA model for two values of the inter-level scattering time, $\tau_0/\tau_{1e-1h} = 1$ and 2, $\tau_{1e-1h} = 0.75ns$.

processes are restricted to the *next* lower level $n \to n - 1$. For $\tau_0 = 0$, the carriers are always in the energetically lowest states; thus the number of carriers describes the micro-state unambiguously. The number of micro-states is thus reduced to $M + 1 = 31$ including the empty dot. The transients for this case are shown in Fig. 3a. The essential features of the experiments are already reproduced. While excited states are strongly populated, the lower levels exhibit a plateau region because they remain completely filled due to instantaneous carrier refill. Higher excited states exhibit increasingly faster asymptotic decay constants compared with that of the ground state (τ_{1e-1h}).

For finite values of τ_0 we consider first the TDA model, where relaxation processes into all lower levels are incorporated (Fig. 3a). The transients exhibit a significant difference from the case $\tau_0 = 0$ only for $\tau_0/\tau_{1e-1h} > 0.1$. The main effects are intensity from excited states remaining at larger delay times, an increase of the asymptotic decay constants of excited states and that the plateau region does not remain flat. It exhibits a slow decay while upper levels are still significantly filled because the refill rate decreases

with decreasing population of all excited states. Using the parameters $\tau_{1e-1h} = 0.75$ ns and $\tau_0 = 0.75$ ns a very good fit of the experimental data at large times (asymptotic slopes of the ground and excited state) is obtained (Fig. 3b). Using $\tau_0 = 1.5$ ns a better overall fit mimicking the decrease of plateau intensities is achieved; however, the decay of the 2e-2h transition comes out too slow.

We conclude for slow inter-level relaxation, $\tau_0/\tau_{1e-1h} \approx 1$. Therefore the asymptotic decay of the first excited state is governed by (0,1,0,0,0) QDs.

In the TDN model, considering only relaxation processes to the next lower level, the transients exhibit a concave bump (Fig. 3a) not observed in the experiment which yields convex transients. Thus the TDN model seems not appropriate, at least not in conjunction with initial complete filling of dots.

In Ref. [10] the experimental data had been fitted with a CRE model and TDN scheme; a value $\tau_0/\tau_{1e-1h} \approx 0.67$ was deducted. From our analysis it becomes clear that because the inter-level scattering time is large and close to the radiative lifetime, the CRE model was able to fit the experimental data with a reasonable value for τ_0.

In summary we have applied a novel concept, master equations for the micro-states, to the description of time-resolved luminescence experiments on multi-level QDs with fast and slow inter-level relaxation. Conventional rate equation models for the ensemble averaged population probabilities are incorrect and largely overestimate the inter-level relaxation time constant if it is small compared to the recombination time constants. More complicated processes than discussed in this work, like Auger recombination, two photon processes, spin dynamics, and effects due to finite temperature (thermal population of excited states by phonon absorption) can be included.

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